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MANUFACTURING OF HIGHER FATTY ACID (C_{6-22}) ESTER OF STEROLS OR RELATED VITAMINS

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[There are no amendments to this invention.]

Brief description of the figure

Figure 1 shows the relationship among the acid value, reactivity, and reaction time of the reaction product.

Detailed explanation of the invention

The solubility of cholesterol, oryzanol, or their derivatives (such as acetyl cholesterol) was significantly increased by adding a fatty acid ester of a higher fatty acid (C_{6-22}) esterol ester or related vitamins such as vitamin D or E to fat and oil in the required amount. The effect can be used for medications, cosmetics, and food.

Esterification of alcohols with fatty acids cannot be easily carried out without a catalyst. In particular, it has been said that esterification of higher alcohols cannot be easily carried out. Inorganic acids, metal compounds such as zinc chloride, tin chloride, or alkali carbonates, or metals such as tin have been used as the catalyst. It is difficult to remove the catalyst after the reaction has ended.

Therefore, it was found by the inventor that higher fatty acid (C_{6-22}) esters of sterols or related vitamins could be

obtained at a high yield in a comparatively short time by adding higher fatty acids (C_{6-22}) or their anhydrides to sterols or to the related vitamins, then heating them to 220-240°C either under reduced pressure or in the presence of an inert gas.

Application Example 1

A fatty acid obtained by distilling rice bran oil (acid value: 202, saponification value: 203, iodine value: 101) (2 mol) was added to β-citrosterol (melting point: 137°C). The mixture was heated at various temperatures in the gaseous nitrogen flow. Samples were taken at different times to measure the acid values. Results are shown in the following.

The ratio of sterols, the above-mentioned vitamins, and higher fatty acids (C_{6-22}) could have been based on equivalent moles in the present invention. However, using one of them at a slightly higher amount than the others was suitable to accelerate the reaction. After the reaction was over, excess component was removed by distillation under reduced pressure or by solvent separation. It was assumed that using a higher fatty acid (C_{6-22}) in excess was convenient for a final treatment. After the reaction was over, the higher fatty acid (C_{6-22}) was removed with an alkali. The reaction was carried out at 150, 200, and 220 to 230°C. The best reactivity was obtained by carrying out the reaction at 220 to 230°C. The reaction product was colored around 245°C or higher, resulting in bad color quality. Result are shown in the attached Figure 1.

Application Example 2

Lauric acid (2 mol, 4 g) was added to stigmasterol (melting point: 169.5-170°C) (1 mol, 3.1 g), followed by heating for about 4 h in the gaseous nitrogen flow (220-230°C), then the excess amount of lauric acid was washed and removed using a caustic soda aqueous solution, followed by washing with water, dehydration, then distillation to remove benzol. Stigmasterol lauric acid ester (5 g) having an ester value of 92.8 (calculated value of stigmasterol lauric acid ester: 93.4) was obtained.

Application Example 3

Palmitic acid (1.5 mol, 3.0 g) was added to 2,2-dehydroergosterol (1 mol, 3.98 g), followed by reacting for 2 h under a reduced pressure of 100 [illegible], then dissolution in ether. The excess palmitic acid was removed by treating with a caustic soda aqueous solution. Ether was removed by washing, dehydrating, then distilling. 2,2-dehydroergosterol palmitic acid ester having an ester value of 86.5 (calculated value: 87.0, 5.2 g) was obtained as a residue.

Application Example 4

Oleic acid (1.5 mol, 4.24 g) was added to γ-tocopherol (1 mol, 4.17 g), followed by heating to carry out a reaction for 2 h under a reduced pressure of 100 [illegible] at 220°C, dissolution in benzol, then treatment using a caustic soda aqueous solution (containing 10% of acetone). Both the excess oleic acid and a very small amount of unreacted γ-tocopherol were

removed, followed by washing with water, dehydration, then distillation. γ-tocopherol oleic acid ester was obtained. Yield 6.54 g (about 96% of calculated value), saponification value: 82.8 (theoretical value: 82.4). The ultraviolet absorption spectrum was measured, resulting in the observation of γ-tocopherol oleic acid ester.

Then, cholesterol (15%) was added, heated, and dissolved in soybean oil, followed by cooling at room temperature, resulting in the initiation of crystallization for about 2 min, followed by solidification for about 2 h. In another experiment, both cholesterol (15%) and the above-mentioned higher fatty acid ester of sterol or vitamin D or E (1%) were added, heated and dissolved, then cooled to room temperature, resulting in the observation of no crystallization after 24 h.

Claim

Manufacturing of higher fatty acid (C_{6-22}) ester of sterols or related vitamins, characterized by adding either a sterol such as β, γ-citrosterol, stigmasterol, ergosterol, or campesterol, or related compounds such as vitamin D (2,2-dihydroergosterol, 7-dehydrocitrosterol, 7-dehydrostigmasterol, or 7-dehydrocholesterol) or vitamin E (α,β-tocopherol) and either a higher fatty acid (C_{6-22}) or its anhydride, followed by heating either under reduced pressure or in the presence of an inert gas flow to 220-240°C to complete esterification, then distillation under reduced pressure, solvent separation, or alkali treatment to remove any unreacted compound.

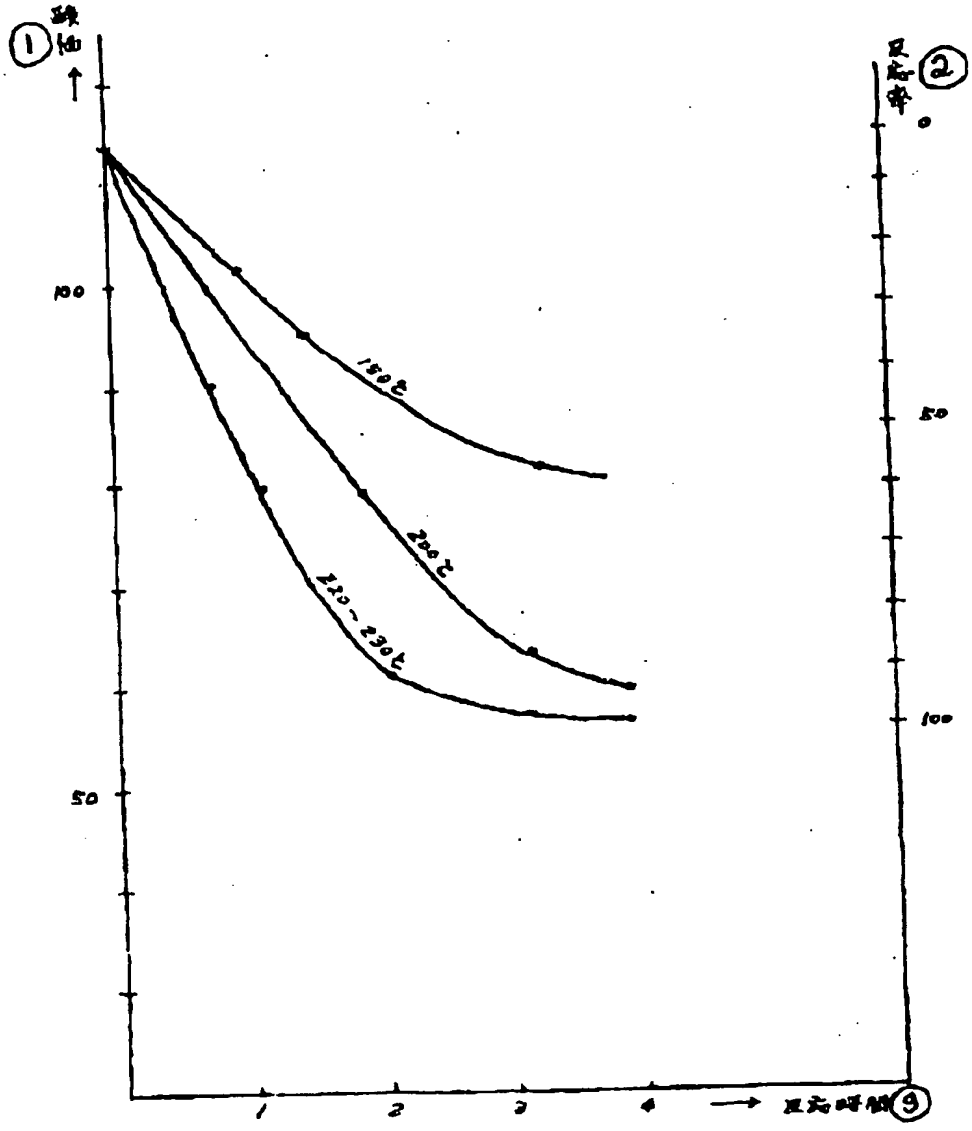

Figure 1

Key: 1 Acid value
2 Reactivity
3 Reaction time